ROTATIONAL EXCITATION IN COLLISIONS BETWEEN TWO RIGID ROTORS: ALTERNATE ANGULAR MOMENTUM COUPLING AND PRESSURE BROADENING OF HCl BY H_2

Sheldon GREEN
Goddard Institute for Space Studies, New York, New York 10025, USA
and Department of Chemistry, Columbia University, New York, New York 10027, USA

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In order to compute relaxation "cross sections" for molecule–molecule collisions it is convenient to employ a coupled angular momentum representation which differs from that generally used. An explicit expression for collision-induced spectral pressure broadening in this representation is given, and this is used to examine the difference between para- and ortho-H_2 for broadening of HCl.

The quantum mechanical description of collision processes can generally be simplified by introducing a total angular momentum representation in which the internal momenta of target and projectile are coupled with the (partial wave) orbital angular momentum of relative motion to yield a total angular momentum. In this representation the hamiltonian for the system will be diagonal in the total momentum, J, and its space-fixed projection, M, and independent of M for each value of J. For the case of rotational excitation of rigid linear molecules by collisions with atoms, the resulting simplifications have been given explicitly in the classic paper of Arthurs and Dalgarno [1].

For the more general case of molecule–molecule collisions, where both target and projectile have internal angular momentum, more than one total angular momentum representation is possible depending on the order in which the momenta are coupled together. However, previous calculations for rotational excitation in collisions between two linear rigid rotors appear to have all used the same coupling scheme (see ref. [2] and references therein): the rotational momenta of target j_1 and projectile j_2 are coupled first to give a resultant j_{12}, and this in turn is coupled to the orbital angular momentum l to give J. In this letter an alternative coupling scheme is presented which provides a more natural description for certain relaxation phenomena.

The traditional coupling scheme implies angular momentum basis functions

$$|(j_1 j_2) j_{12} lJM\rangle = \sum_{m_1 m_2 m_{12} m} (j_1 m_1 j_2 m_2 | j_1 j_2 j_{12} m_{12})(j_{12} m_{12} l m | j_{12} l J M) |j_1 m_1\rangle |j_2 m_2\rangle |lm\rangle \,, \tag{1}$$

where $(...|...)$ is a Clebsch–Gordan vector-coupling coefficient [3]. In this representation the target and projectile are treated on an equal footing. In many experiments, however, one measures rotational relaxation of one molecular species (the "system") due to collisions with some other molecules (the "bath"). In describing such relaxation phenomena it is most convenient [4] to first couple the internal angular momentum of the bath molecule j_2 with its translational momentum l to obtain a resultant $\bar{j}$, and this in turn is coupled with the momentum of the system molecule j_1 to yield J. The basis functions in this representation are

$$|j_1 (j_2 l) \bar{j} JM\rangle = \sum_{m_1 m_2 \bar{m} m} (j_2 m_2 l m | j_2 l \bar{j} \bar{m})(\bar{j} \bar{m} j_1 m_1 | \bar{j} j_1 J M) |j_1 m_1\rangle |j_2 m_2\rangle |lm\rangle \,. \tag{2}$$

These two representations are related, as usual, by a unitary transformation. Because the recoupling of three angular momenta as described in eqs. (1) and (2) *defines* the 6-j symbol one can write immediately [3]

$$|j_1(j_2 l)\bar{j}JM\rangle = \sum_{j_{12}} [(2\bar{j}+1)(2j_{12}+1)]^{1/2}(-1)^{j_1+j_2+l+J}\begin{Bmatrix} j_1 & j_2 & j_{12} \\ l & J & \bar{j} \end{Bmatrix}|(j_1 j_2)j_{12}lJM\rangle , \tag{3}$$

and also

$$|(j_1 j_2)j_{12}lJM\rangle = \sum_{\bar{j}}[(2\bar{j}+1)(2j_{12}+1)]^{1/2}(-1)^{j_1+j_2+l+J}\begin{Bmatrix} j_1 & j_2 & j_{12} \\ l & J & \bar{j} \end{Bmatrix}|j_1(j_2 l)\bar{j}JM\rangle . \tag{4}$$

Matrix elements — including the potential matrix elements in the close-coupling formulation and the scattering **S** matrix — can readily be transformed from one representation to the other. For example‡

$$\langle j_1(j_2 l)\bar{j}J|S|j_1'(j_2' l')\bar{j}'J\rangle = \sum_{j_{12}j_{12}'} [(2j_{12}+1)(2j_{12}'+1)(2\bar{j}+1)(2\bar{j}'+1)]^{1/2}$$

$$\times \begin{Bmatrix} j_1 & j_2 & j_{12} \\ l & J & \bar{j} \end{Bmatrix}\begin{Bmatrix} j_1' & j_2' & j_{12}' \\ l' & J & \bar{j}' \end{Bmatrix}\langle (j_1 j_2)j_{12}lJ|S|(j_1' j_2')j_{12}'l'J\rangle . \tag{5}$$

Because the transformation is unitary, the expression for the integrated, degeneracy averaged cross sections has the same form in both representations:

$$\sigma(j_1' j_2' \leftarrow j_1 j_2) = \{\pi/[(2j_1+1)(2j_2+1)k^2]\} \sum_{Jj_{12}'j_{12}l'l} (2J+1)|\langle (j_1' j_2')j_{12}'l'J|T|(j_1 j_2)j_{12}lJ\rangle|^2$$

$$= \{\pi/[(2j_1+1)(2j_2+1)k^2]\} \sum_{J\bar{j}'\bar{j}l'l} (2J+1)|\langle j_1'(j_2' l')\bar{j}'J|T|j_1(j_2 l)\bar{j}J\rangle|^2 , \tag{6}$$

where the transition operator $\mathbf{T} = \mathbf{1} - \mathbf{S}$, and k is the wavevector of relative motion.

As an example of the utility of this coupling scheme for relaxation processes, we consider explicitly the "cross section" which describes collision-induced spectral pressure broadening. Following Ben-Reuven [4] one can construct a rotationally invariant form by coupling the tensor character of the radiation, the angular momentum of the system, and the *total* angular momentum of the bath.

$$\sigma(j_a' j_b'; j_a j_b; j_2' j_2; E) = (\pi/k^2) \sum_{J_a J_b \bar{j}'\bar{j} l' l} (2J_a+1)(2J_b+1)(-1)^{j_a - j_a' + \bar{j} - \bar{j}'}\begin{Bmatrix} j_a' & n & j_b' \\ J_b & \bar{j}' & J_a \end{Bmatrix}\begin{Bmatrix} j_a & n & j_b \\ J_b & \bar{j} & J_a \end{Bmatrix}$$

$$\times [\delta(\bar{j},\bar{j}')\delta(l',l) - \langle j_b' j_2' l' \bar{j}' J_b|S(E_b)|j_b j_2 l \bar{j} J_b\rangle^* \langle j_a' j_2' l' \bar{j}' J_a|S(E_a)|j_a j_2 l \bar{j} J_a\rangle] , \tag{7}$$

where n is the tensor rank of the radiation (1 for dipole transitions and 2 for Raman spectra); subscripts a and b refer to the initial and final *spectroscopic* levels of the system; unprimed and primed momenta correspond to values before and after collision; and

$$E = E_a - E_{j_a} - E_{j_2} = E_b - E_{j_b} - E_{j_2} = 2\mu k^2 , \tag{8}$$

where μ is the reduced mass of the collision. This cross section has been summed and *not* averaged over the degenerate magnetic quantum levels of the bath molecules. To compare with experiment these cross sections must be averaged over initial bath conditions — generally a Boltzmann distribution in E and fractional probability of finding the bath molecule initially in j_2 — and summed over all possible final bath levels j_2'. As noted by Shafer and Gordon [5] for non-overlapping spectral lines, only the "diagonal" $j_a = j_a'$ and $j_b = j_b'$ terms are needed; however, all energetically important $j_2' j_2$ elements will still be necessary.

‡ The parity factor has been dropped here since there is no coupling between basis functions with different $(j_1 + j_2 + l + J)$ parity.

To illustrate the application of this formalism, some results from a study of HCl–H_2 collisions are presented here. This study was undertaken to consider differences between para- and ortho-H_2 as a collision partner since this is relevant to the interpretation of certain radioastroastronomical observations. At the low temperatures of interstellar space, para-H_2 is in its lowest, $j = 0$ level and ortho-H_2 is in $j = 1$. The $j = 0$ level, being spherically symmetric, does not exhibit a permanent quadrupole moment, and hence the long-range dipole-quadrupole part of the intermolecular potential is quenched for para-H_2. (See, e.g. Green and Thaddeus [6].) The HCl–H_2 interaction was adapted from that for HCl–He [7]. A similar procedure was shown to have some validity for CO–H_2 [6]; unlike ref. [6], no adjustments have been made here for the differing well depths or for the "size" of H_2 relative to He. Thus, the HCl–H_2 interaction is assumed to be the HCl–He interaction of ref. [7] plus the asymptotic dipole–quadrupole interaction which is cut off smoothly, but rapidly in the region of the minimum. While this may not be extremely accurate, it undoubtedly mimics the dominant features of the potential and should be adequate to document the differences between excitation by para- and ortho-H_2.

Using this interaction potential, close coupling scattering calculations were done. These employed expansion basis sets of HCl rotational levels $j_1 = 0$ through $j_1 = 4$ and a *single* H_2 level, $j_2 = 0, 1,$ *or* 2. The close coupling equations were solved using the standard angular momentum coupling, eq. (2), and the S-matrices were transformed via eq. (5) to compute pressure broadening cross sections. Results for state-to-state integral cross sections are given in tables 1 and 2, and for pressure broadening cross sections in table 3.

Table 1
Close coupling cross section (in Å^2) for the process HCl(j_1) + $H_2(j_2)$ → HCl(j_1') + $H_2(j_2)$. The total energy is fixed such that the relative kinetic energy is 200 cm^{-1} minus the initial rotational energy of the HCl. Also given is J_{max}, the highest total momentum retained to obtain converged cross sections

HCl(j_1 → j_1')		$H_2(j_2 = 0)$	$H_2(j_2 = 1)$	$H_2(j_2 = 2)$
0	1	3.01	10.54	8.59
0	2	1.28	1.48	1.46
0	3	1.16	1.16	1.16
1	2	2.67	7.91	6.62
1	3	0.83	0.90	0.91
2	3	2.40	4.54	4.08
J_{max}		28	50	46

Table 2
The same as table 1 except the collision energy is 300 cm^{-1} minus the initial rotational energy of the HCl

HCl(j_1 → j_1')		$H_2(j_2 = 0)$	$H_2(j_2 = 1)$
0	1	3.11	8.15
0	2	1.65	1.78
0	3	1.12	1.14
0	4	0.53	0.54
1	2	2.76	6.56
1	3	1.21	1.24
1	4	0.65	0.66
2	3	2.67	5.50
2	4	0.93	0.93
J_{max}		32	58

Table 3
Close coupling cross sections (in Å^2) for pressure broadening of pure rotational lines of HCl due to collisions with H_2 in various rotational levels

Collision energy (cm^{-1})	Spectral line	$H_2(j = 0)$	$H_2(j = 1)$	$H_2(j = 2)$
200	0–1	5.6	13.3	11.4
	1–2	5.7	12.6	10.9
300	0–1	6.5	11.9	10.2
	1–2	6.6	11.8	10.3

As anticipated, a significant difference is seen between H_2 in the $j_2 = 0$ level and H_2 with $j_2 > 0$. In particular, in the former case, where the dipole–quadrupole interaction is quenched, cross sections for $\Delta j_1 = +1$ transitions of HCl are a factor of 2 to 3 smaller. This is also reflected in the smaller pressure broadening cross sections which are found when the H_2 perturbers are restricted to the $j_2 = 0$ level. This behavior might be slightly modified by other terms in the HCl–H_2 interaction which have not been included here – e.g., the long-range quadrupole–quadrupole interaction or the short-range H_2 anisotropies – but these are expected to be much smaller effects and should not change the qualitative picture found here.

It is noteworthy that the collision-induced spectral pressure broadening of HCl by cold para-H_2 (i.e. all molecules in $j = 0$) is predicted to be measureably different from that due to ortho-H_2 or the normal thermal para–ortho mixture. This effect has apparently not been looked for, but such experiments would provide an interesting test of these calculations.

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